

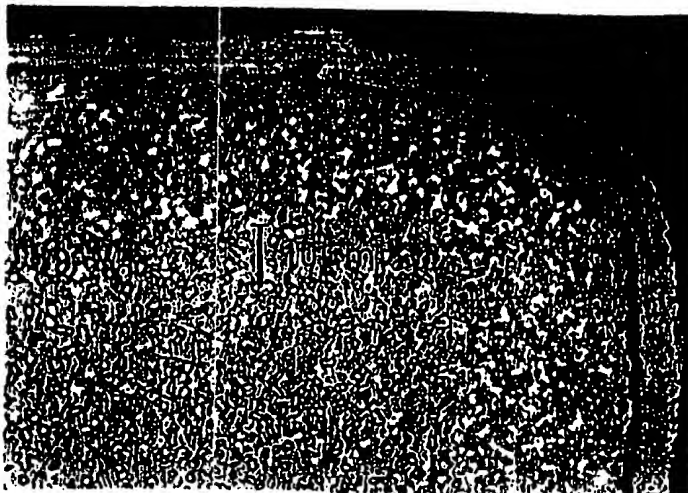
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(21) International Application Number: PCT/SE97/01690 (22) International Filing Date: 9 October 1997 (09.10.97) (30) Priority Data: 9603758-5 11 October 1996 (11.10.96) SE (71) Applicant (for all designated States except US): SANDVIK AB (publ) [SE/SE]; S-811 81 Sandviken (SE). (72) Inventors; and (75) Inventors/Applicants (for US only): LINDSKOG, Per [SE/SE]; Staffan Stallares Väg 17, S-125 35 Älvsjö (SE). GUSTAFSON, Per [SE/SE]; Stuvstavägen 7, S-141 40 Huddinge (SE). (74) Agents: ÖSTLUND, Alf et al.; Sandvik AB, Patent Dept., S-811 81 Sandviken (SE).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: METHOD OF MAKING CEMENTED CARBIDE WITH BINDER PHASE ENRICHED SURFACE ZONE**(57) Abstract**

The present invention relates to method of making a cemented carbide insert, comprising a cemented carbide substrate and a coating. The substrate contains WC and cubic carbonitride phase in a binder phase based of Co and/or Ni and has a binder phase enriched surface zone essentially free of cubic phase. The binder phase enriched surface zone prevails over the edge. By sintering in an atmosphere essentially consisting of nitrogen the thickness of the binder phase enriched zone can be controlled.



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Method of making cemented carbide with binder phase
enriched surface zone

The present invention relates to coated cemented
5 carbide inserts with unique edge security in sticky work
piece materials such as stainless steel, achieved with a
binder phase enriched surface zone extending over the
edge.

Coated cemented carbide inserts with binder phase
10 enriched surface zone are today used to a great extent
for machining of steel and stainless materials. Thanks
to the binder phase enriched surface zone, an extension
of the application area for the cutting material has
been obtained.

15 Methods or processes to make cemented carbide
containing WC, cubic phase (gamma-phase) and binder
phase with binder phase enriched surface zones are known
through a number of patents and patent application.
According to e.g. US Patents 4,277,283 and 4,610,931
20 nitrogen containing additions are used and sintering
takes place in vacuum whereas according to US Patent
4,548,786 the nitrogen is added in gas phase. Hereby in
both cases a binder phase enriched surface zone
essentially free of cubic phase is obtained. US Patent
25 4,830,939 describes a binder phase enrichment obtained
through decarburization after the sintering whereby a
binder phase enrichment is obtained which also contains
cubic phase.

It is well known in the art that the thickness of
30 the binder phase enriched zone decreases towards sharp
corners, such as the cutting edge of a cutting insert,
and that a brittle binder phase depleted zone, enriched
in cubic phase, is present in the edge area and often
limits the use of binder phase enriched cemented

carbides especially in work piece materials with high demands on edge toughness.

However, the edges of a cutting insert has to be edge rounded to a certain radius of the order of 50-100
5 μm or less in order to be useful. The edge rounding is generally made after sintering by an edge rounding operation. In this operation the thin outermost binder phase enriched zone is completely removed and the hard, brittle area is exposed. As a result a hard but brittle
10 edge is obtained resulting in an increased risk for problems with brittleness in the edge particularly in applications demanding high edge toughness.

One method of reducing this drawback of binder phase enriched sintered cemented carbides is described in US
15 5,484,468. This method is, however, not sufficient in very difficult work piece materials such as austenitic stainless steel and may result in an unwanted decrease in the deformation resistance.

A method of maintaining the binder phase enriched
20 zone in the edge portion of a cemented carbide insert is disclosed in EP-A-0569696. According to this application this effect is obtained if Zr and/or Hf is present in the cemented carbide.

According to Swedish Patent application SE 9501383-5
25 the thickness of the binder phase enriched surface zone can be maintained over the edge also in cemented carbide free of Hf and Zr if certain conditions are fulfilled particularly with regard to the titanium and nitrogen content within the cubic phase as well as the overall
30 carbon content. A favourable influence on the edge toughness in sticky materials such as austenitic stainless steel can thereby be obtained. However, the binder phase enriched zones according to this application often becomes too deep and difficult to
35 control.

It is an therefore an object of the present invention to provide a method of making a cemented carbide insert allowing a better control of the thickness of the binder phase enriched zone.

5 According to the presently claimed invention there is provided a cemented carbide insert, comprising a cemented carbide substrate and a coating. The substrate contains WC and cubic carbonitride phase in a binder phase based of Co and/or Ni and has a binder phase
10 enriched surface zone essentially free of cubic phase. The binder phase enriched surface zone prevails over the edge. As a result an insert according to the invention has improved edge toughness and is particularly useful for machining of sticky work piece materials such as
15 stainless steel. (Although the cubic phase is essentially a carbonitride phase the material is herein referred to as a cemented carbide.)

Fig. 1 shows in 800X the binder phase enriched zone under a cutting edge rounded to a 50 μm radius in a
20 coated cemented carbide according to the invention.

It has now surprisingly been found that by performing part of the sintering under nitrogen pressure the thickness of the binder phase enriched surface zone can be controlled with gradient prevailing in the
25 vicinity of the edge.

The invention, thus, relates to a method of making cutting inserts comprising a cemented carbide substrate consisting of a binder phase of Co and/or Ni, WC and a cubic carbonitride phase with a binder phase enriched
30 surface zone essentially free of cubic phase and a coating. A powder mixture containing WC, 6-14 atom-%, preferably 8-11 atom-% binder phase and 3-8 atom-%, preferably 4-6 atom-% of Ti and at least one of Ta and Nb such that the $\text{Ti}/(\text{Ta}+\text{Nb})$ atomic ratio is >2 ,
35 preferably >3 . Ta and/or Nb is/are added as carbides

whereas Ti is added as TiC, TiCN and/or TiN in such proportions that the nitrogen content of the carbonitride phase expressed as x in the formula, $(\text{Ti}, \text{Nb}, \text{Ta}) (\text{N}_x, \text{C}_{1-x})$ shall be >0.2 , preferably $0.3-0.4$.

5 The powder mixture is mixed with pressing agent and possibly carbon such that the carbon content is $0-0.15$, preferably $0.05-0.15$, weight-%, above the stoichiometric content and the mixture is milled and dried to obtain a powder material. Next, the powder material is compacted
10 and sintered. During heating to sintering nitrogen gas may be supplied to the furnace at $0-500$ mbar, preferably $10-40$ mbar, in order to prevent denitrification prior to pore closure at temperatures above 1200°C . Sintering is performed at a temperature of $1380-1520^\circ\text{C}$, in a
15 protective atmosphere consisting essentially of nitrogen, the nitrogen pressure adjusted to impede gradient growth, with a period of sintering in an atmosphere without nitrogen, the time of this period adjusted to obtain the gradient zone depth desired. The
20 nitrogen pressure required to impede gradient growth depends on composition of the carbide body, sintering temperature and on the furnace used. The time required in atmosphere without nitrogen addition depends on sintering temperature and furnace used. It is within the
25 purview of the skilled artisan to determine whether the requisite binder phase enrichment has been obtained and to modify the sintering conditions in accordance with the present specification, if desired, to effect the desired binder phase enrichment.

30 Cooling can be performed according to standard practice or as disclosed in US 5,484,468. After conventional post sintering treatments including edgerounding a hard, wear resistant coating according to above is applied by CVD-, PVD- or MT-CVD-technique.

The present invention also relates to a cutting insert comprising a cemented carbide substrate with a binder phase enriched surface zone and a coating, said substrate consisting of a binder phase of Co and/or Ni, WC and a cubic carbonitride of W, Ti and at least one of the metals Ta, Nb, Mo, V, or Cr with a binder phase enriched surface zone being essentially free of cubic phase.

Preferably the cemented carbide contains 6-14 atom-%, most preferably 8-11 atom-%, binder phase, 3-8 atom-%, most preferably 4-6 atom-%, of Ti and at least one of Ta and Nb and rest WC. The average WC grain size shall be between 1.0 and 4 μm , preferably between 1.5 and 3 μm . The Ti/(Ta+Nb) atomic ratio in the carbonitride phase shall be >2 , preferably >3 , with a nitrogen content expressed as x in the formula, $(\text{Ti}, \text{Nb}, \text{Ta})(\text{N}_x, \text{C}_{1-x})$ shall be >0.2 , preferably between 0.3 and 0.4. The depth of the binder phase enriched surface zone close to the edge increases with increased titanium and nitrogen content within the cubic phase and with increased overall carbon content. The maximum nitrogen content that can be used in practice is mainly limited by the increased tendency for A and B type of porosity with increased nitrogen content. However, the maximum nitrogen content can be extended over the above stated limit if the sintering is performed in an inert atmosphere under high pressure. The maximum carbon content that can be used in practice is mainly limited by an increased tendency for carbon precipitation in the binder phase enriched surface zone, reduced coating adhesion and reduced deformation resistance. The carbon content shall correspond to a C-porosity better than C08, preferably C00 just below carbon saturation.

The thickness of the binder phase enriched surface zone shall be

1. below a flat surface 15-45 μm , preferably 25-35 μm
2. close to a sharp edge, before edge rounding, measured perpendicular to the same flat surface as in 1. above, 0.5-1.2 times the gradient zone in 1. above, preferably 0.67-1.2 times the gradient zone in 1. above.
3. at the edge after edge rounding 5-30 μm , preferably 10-25 μm .

10 The gradient zone depth close to the edge depends on the geometry, a blunt, 90 degrees or more, geometry giving deeper gradient zones.

Inserts according to the invention shall preferably have a coating of TiC, TiCN and/or TiN with a total
15 coating thickness of 3-10 μm , most preferably 4-8 μm , possibly in combination with an Al_2O_3 coating with a thickness of 1-4 μm , most preferably 1.5-3 μm . Other coatings known in the art can also be used such as
20 nitride, carbonitride, oxide or boride of at least one metal of the groups IVb, VB and VIB of the periodic table and/or aluminium oxide by known CVD-, PVD- or MT-CVD-methods.

25 Example 1 (according to invention)

From a powder mixture comprising 1.69 weight-% TiC, 1.28 weight-% TiN, 1.21 weight-% TaC, 0.76 weight-% NbC, 7.5 weight-% Co, and balance WC with 0.12 weight-% overstoichiometric carbon content, turning inserts
30 CNMG120408 were pressed. The inserts were sintered with H_2 up to 450°C for dewaxing, further in vacuum to 1200°C, and after that with a protective gas of 40 mbar nitrogen up to 1380°C the furnace was then evacuated and filled with nitrogen to 60 mbar and heated to sintering
35 temperature, 1450°C, and held there for 60 minutes,

during these 60 minutes the furnace was evacuated for 15 min and then refilled with nitrogen.

The structure in the surface of the cutting inserts consisted of a 30 μm thick binder phase enriched zone
5 below the flat flank face with a minimum if 25 μm close to the edge.

Example 2 (according to invention)

From a powder mixture comprising 1.69 weight-% TiC,
10 1.28 weight-% TiN, 1.21 weight-% TaC, 0.76 weight-% NbC, 7.5 weight-% Co, and balance WC with 0.12 weight-% overstoichiometric carbon content, turning inserts CNMG120408 were pressed. The inserts were sintered with H₂ up to 450°C for dewaxing, further in vacuum to
15 1200°C, and after that with a protective gas of 40 mbar nitrogen up to 1380°C the furnace was then evacuated and filled with nitrogen to 200 mbar heated to sintering temperature, 1450°C, and held there for 10 minutes and then cooled to 1380°C, evacuated and held at 1380°C for
20 50 minutes and then cooled.

The structure in the surface of the cutting inserts consisted of a 33 μm thick binder phase enriched zone below the flat flank face with a minimum if 23 μm close to the edge.

25

Example 3 (prior art).

From a powder mixture comprising 1.69 weight-% TiC, 1.28 weight-% TiN, 1.21 weight-% TaC, 0.76 weight-% NbC, 7.5 weight-% Co, and balance WC with 0.12 weight-%
30 overstoichiometric carbon content, turning inserts CNMG120408 were pressed. The inserts were sintered with H₂ up to 450°C for dewaxing, further in vacuum to 1200°C, and after that with a protective gas of 40 mbar nitrogen up to 1380°C the furnace was then evacuated and
35 filled with argon to 40 mbar heated to sintering

temperature, 1450°C, and held there for 1 hour and then cooled.

The structure in the surface of the cutting inserts consisted of a 46 µm thick binder phase enriched zone
5 below the flat flank face with a minimum of 30 µm close to the edge.

Example 4 (prior art)

From a powder mixture comprising 1.69 weight-% TiC,
10 1.28 weight-% TiN, 1.21 weight-% TaC, 0.76 weight-% NbC,
7.5 weight-% Co, and balance WC with 0.12 weight-%
overstoichiometric carbon content, turning inserts
CNMG120408 were pressed. The inserts were sintered with
H₂ up to 450°C for dewaxing, further in vacuum to 1380°C
15 the furnace was then filled with argon to 40 mbar heated
to sintering temperature, 1410°C, and held there for 1
hour and then cooled.

The structure in the surface of the cutting inserts consisted of a 40 µm thick binder phase enriched zone
20 below the flat flank face with a minimum of 26 µm close to the edge.

Example 5 (comparative)

From a powder mixture comprising 1.69 weight-% TiC,
25 1.28 weight-% TiN, 1.21 weight-% TaC, 0.76 weight-% NbC,
7.5 weight-% Co, and balance WC with 0.12 weight-%
overstoichiometric carbon content, turning inserts
CNMG120408 were pressed. The inserts were sintered with
H₂ up to 450°C for dewaxing, further in vacuum to
30 1200°C, and after that with a protective gas of 40 mbar
nitrogen up to 1380°C the furnace was then evacuated and
filled with nitrogen to 100 mbar heated to sintering
temperature, 1450°C, and held there for 1 hour and then
cooled.

The structure in the surface of the cutting inserts consisted of a 26 μm thick binder phase enriched zone below the flat flank face with a minimum of 12 μm close to the edge.

5

Examples 1 and 2 show that it is possible to control the depth of the gradient zone without losing the desired gradient in the vicinity of the edge as in example 5. Examples 3 and 4 show that the gradient zone may grow excessively without nitrogen addition under a part of the sintering.

10

Claims

1. Method of making a cutting insert comprising a cemented carbide substrate with a binder phase enriched surface zone and a coating, said substrate consisting of
5 a binder phase of Co and/or Ni, WC and a cubic carbonitride phase, said binder phase enriched surface zone being essentially free of said cubic carbonitride phase and with an essentially constant thickness around the insert characterised in forming a powder mixture
10 containing WC, 6-14 atom-%, preferably 8-11 atom-%, binder phase and 3-8 atom-%, preferably 4-6 atom-%, of Ti and at least one of Ta and Nb such that the Ti/(Ta+Nb) atomic ratio is >2 , preferably >3 , Ta and/or Nb being added as carbide and Ti as carbide, nitride
15 and/or carbonitride in such proportions that the nitrogen content of the carbonitride phase expressed as x in the formula, $(\text{Ti}, \text{Nb}, \text{Ta})(\text{N}_x, \text{C}_{1-x})$, is >0.2 , preferably 0.3-0.4

adding to said powder mixture pressing agent and
20 possibly carbon such that the carbon content is 0-0.15 weight-% above the stoichiometric content

milling and drying the mixture to obtain a powder material

compacting and sintering the powder material whereby
25 between 1200°C and pore closure nitrogen gas may be supplied to the furnace at 0-500 mbar, preferably 10-40 mbar, after which sintering is performed at a temperature of 1380-1520°C, preferably 1410-1450°C, in a
protective atmosphere consisting essentially of
30 nitrogen, the nitrogen pressure adjusted to impede gradient growth, with a period of sintering in an atmosphere without nitrogen, the time of this period adjusted to the gradient zone desired, followed by cooling according to standard practice

applying conventional post sintering treatments including edgerounding and

forming a hard, wear resistant coating of single or multiple layers of at least one carbide, nitride, carbonitride, oxide or boride of at least one metal of the groups IVb, VB and VIB of the periodic table and/or aluminium oxide by known CVD-, PVD- or MT-CVD-technique.

2. Cutting insert for machining of sticky work piece materials such as stainless steel comprising a cemented carbide substrate with a binder phase enriched surface zone and a coating, said substrate consisting of a Co binder phase, WC and a cubic carbonitride phase of W and at least one of the metals Ti, Ta, Nb, Mo, V, or Cr said binder phase enriched surface zone being essentially free of said cubic phase characterised in a thickness of said binder phase enriched surface zone of 15-45 μm on a flat surface of said insert and of 5-30 μm in the cutting edge.

3. Cutting insert according to claim 2 characterised in said substrate consisting of 6-14 atom-% binder phase, 3-8 atom-%, preferably 4-6 atom-% of Ti and at least one of Ta and Nb such that the Ti/(Ta+Nb) atomic ratio is >2 and that the nitrogen content of the carbonitride phase expressed as x in the formula, $(\text{Ti}, \text{Nb}, \text{Ta})(\text{N}_x, \text{C}_{1-x})$, is >0.2 .

4. Cutting insert according to claim 3 characterised in said Ti/(Ta+Nb) atomic ratio >3 .

5. Cutting insert according to claims 3 or 4 characterised in $0.3 < x < 0.4$.

6. Cutting insert according to any of claims 2, 3, 4 or 5 characterised in said coating consisting of at least one of TiC, TiCN or TiN with a total coating thickness of 3-10 μm .

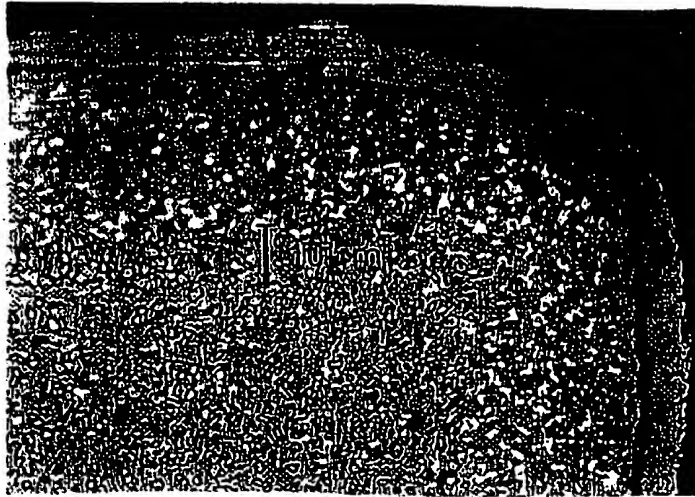


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/01690

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C22C 29/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9317140 A1 (SANDVIK AB), 2 Sept 1993 (02.09.93), page 2, line 14 - page 6, line 12 --	1-6
X	US 4649084 A (THOMAS E. HALE ET AL), 10 March 1987 (10.03.87), column 2, line 42 - column 3, line 2; column 9, line 19 - column 10, line 56, figure 5 --	1-6
X	US 4548786 A (WARREN C. YOHE), 22 October 1985 (22.10.85), whole document --	1-6

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

12 February 1998

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/01690

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5484468 A (ÅKE ÖSTLUND ET AL), 16 January 1996 (16.01.96), column 1, line 1 - column 2, line 27; column 2, line 65 - column 4, line 17	2-6
A	---	1
A	US 4277283 A (MASAAKI TOBIOKA ET AL), 7 July 1981 (07.07.81) -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

03/02/98

International application No.

PCT/SE 97/01690

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9317140 A1	02/09/93	BR 9305926 A CA 2130544 A CN 1079179 A EP 0597012 A EP 0627016 A IL 104747 A JP 6509698 T JP 7503996 T SE 9200530 D US 5549980 A US 5578886 A	26/08/97 02/09/93 08/12/93 18/05/94 07/12/94 31/10/96 27/10/94 27/04/95 00/00/00 27/08/96 26/11/96
US 4649084 A	10/03/87	CA 1278173 A EP 0200991 A,B JP 62001853 A	27/12/90 12/11/86 07/01/87
US 4548786 A	22/10/85	AU 568538 B AU 2612884 A JP 60036635 A	07/01/88 01/11/84 25/02/85
US 5484468 A	16/01/96	EP 0682580 A IL 108560 A JP 8506620 T SE 9300376 A WO 9417943 A	22/11/95 20/11/97 16/07/96 06/08/94 18/08/94
US 4277283 A	07/07/81	JP 1147696 C JP 54087719 A	26/05/83 12/07/79